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In(III) and Sc(III) based coordination polymers derived from rigid benzimidazole-5,6-dicarboxylic acid: Synthesis, crystal structure and catalytic property

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1. Introduction

The development of new heterogeneous Lewis acid catalysts has become one of the main goals of green synthetic chemistry [1]. Currently, coordination polymers (CPs) as heterogeneous catalysts are receiving increasing attention [2] not only due to they possess extensive tunability, but also for their highly regular catalytic sites, which represent a unique opportunity to design CPsbased heterogeneous catalysts [3]. Compared to conventional homogeneous catalysts, CPs as heterogeneous catalysts have many advantages, including separation and recovery, selectivity, higher yield, low toxicity, and so on [4]. Generally, one promising point for CPs-based catalysis is the presence of active metal centers, that are coordinatively unsaturated metal centers, in the structure, which may exhibit Lewis acidity and associated catalytic functionality [5]. For example, Garcia et al. reported that Fe(BTC) catalyzed Claisen Schmidt condensation leading to chalcone in 98% yield [6]. Long et al. shown that Mn₃[(Mn₄Cl)₃(BTT)₈(CH₃OH)₁₀]₂ catalyzed cyanosilylation of aromatic aldehydes and Mukaiyama-aldol reaction with excellent size-selectivity effect [7]. Monge et al. prepared a mesoporous In₃O(btb)₂(HCOO)(L), which was reused in up to 10

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ABSTRACT

Two new coordination polymers (CPs), $[InCl(H_2bidc)_2(H_2O)]_n$ (1) and $[Sc(Hbidc)(OH)(H_2O)]_n$ (2) $(H_3bidc = benzimidazole-5,6-dicarboxylic acid)$ were synthesized through a solvothermal approach. 1 exhibits a 1D infinite chain, which further constructs a 3D supramolecular framework via hydrogen bonds. 2 features a 3D supramolecular framework consisting of left- and right-handed chiral layers, which contain the left- and right-handed chiral spiral chains. The adjacent layers stack through π - π stacking interactions between benzene and imidazole rings. 1 exhibits excellent catalytic reactivity for the Strecker reaction and can be recycled four consecutive reactions with more than 95% conversion yields.

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cycles without significant loss of activity [8]. However, finding a way to give rise birth to accessible active metal centers is still a challenge in the construction of CPs.

To obtain CPs with catalytic effective sites, various metallic cations were tested, especially, In(III) or Sc(III). The main reason is that some In(III) or Sc(III) usually more easily adopt a lower six coordination number, which can provide open Lewis acid effective sites [9] for catalysis of various organic reactions [10]. For instance, [In(popha)(2,2'-bipy)]·3H₂O was found to be a highly reactive, recyclable, Lewis acid catalyst, which allowed the efficient synthesis of α -aminoacyl amides in Ugi 4-component (U-4CR) reaction [11]. [Sc₂(C₁₀H₆S₂O₆)(OH)₄]_n as bifunctional catalysts presented particularly good activity for the oxidation of sulfides and can be recycled several consecutive reactions without any loss of activity or selectivity [12].

As is well known, α -aminonitriles are key skeletons of some biologically natural products such as α -amino acids and their derivatives [13]. Up to now, the Strecker reaction of aldimines and trimethylsilyl cyanide (TMSCN) is the most effective method to produce these compounds. Previously, this reaction has been successfully catalyzed by various Lewis acid and Lewis base catalysts. However, there are some problems such as in separation, recovery and disposal of spent catalysts for the Strecker reaction [14]. Moreover, in recent years, Strecker reaction was successfully catalyzed by CPs that presented outstanding catalytic activity. Gandara et al. prepared new CPs $[In_xGa_{1-x}(O_2C_2H_4)_{0.5}(hfipbb)]$, which showed how the activity of a heterogeneous catalyst can be controlled by modulating the ratio of different metals occupying the same crystallographic position of the framework in one-pot Strecker reaction [15]. Ji et al. reported that Cu-CPs, featuring Lewis acid-type catalytic sites, as very efficient and reusable catalysts, were used for the Strecker reaction of various aldimines [16].

In the process of construction and structural tuning of CPs, organic ligand plays a crucial role. Benzimidazole-5,6-dicarboxylic acid (H₃bidc) as a bridging ligand possesses two carboxyl groups, which can be partial or completely deprotonated, inducing rich coordination modes and allowing interesting structures. H₃bidc has been validated to be a proper polydentate bridging ligand for the formation of multidimensional CPs [17]. Here, based on the H₃bidc ligand, we prepare two new In(III)/Sc(III)-based CPs, [InCl(H₂bidc)₂(H₂O)]_n (**1**) and $[Sc(Hbidc)(OH)(H_2O)]_n$ (**2**). **1** features infinite 1D chains and is constructed to a 3D supramolecular framework via hydrogen bonds. 2 shows a 3D supramolecular structure, built from left- and right-handed chiral layers along the *c* axis with the left- and right-handed chiral spiral chains. Interactions of π - π stacking between benzene ring and imidazole rings make the 3D supramolecular more stable. The heterogeneous catalytic activities of CPs 1 and 2 for the Strecker reaction of various aldimines under mild condition have also been investigated. 1 displays good catalytic capability for heterogeneous Strecker reaction with more than 95% conversion yields after four consecutive runs.

2. Experimental

2.1. Materials and instrumentation

All chemicals were obtained from commercial sources and used without further purification. Powder X-ray diffraction (PXRD) data were obtained using SHIMADAZU XRD-6000 diffractometer with Cu Ka radiation ($\lambda = 1.5418$ Å), with a step size and count time of 0.06° and 6 s, respectively. Infrared spectra (IR) were recorded on a Nicolet Impact 410 spectrometer between 400 and 4000 cm⁻¹ using the KBr pellet method. Thermogravimetric analysis (TGA) was conducted on a Perkin-Elmer TGA 7 thermogravimetric analyzer with a heating rate of 10 °C min⁻¹ from room temperature to 800 °C. Elemental analysis was conducted on a Perkin Elmer 2400 elemental analyzer. ¹H NMR spectra were measured with a Bruker Avance 400 console at a frequency of 400 MHz.

2.2. Synthesis

2.2.1. Synthesis of $[InCl(H_2bidc)_2(H_2O)]_n$ (1)

A mixture of H₃bidc (0.0824 g, 0.4 mmol), InCl₃·4H₂O (0.2 ml, 0.1 M) was added to CH₃CN (4 ml), HNO₃ (0.4 ml, 1 M) and H₂O (1 ml) in a 23 ml Teflon-lined autoclave and then heated under autogenous pressure at 120 °C for 24 h, then cooled to room temperature under ambient conditions. Colorless block crystals were obtained by filtration and washed with distilled water, and dried in air. Yield: 85% for 1 (based on InCl₃·4H₂O). Elemental analysis (%) for 1: *Anal.* Calc. C, 37.47; H, 1.73; N, 9.71; Found: C, 37.35; H, 1.55; N, 9.78. IR (KBr pellet, cm⁻¹) for 1 (4000–400 cm⁻¹): 3254 (s), 1594 (s), 1384 (s), 1329 (s), 1035 (m), 1235 (m), 921 (w), 847 (w), 786 (s), 639 (m), 500 (m) (Fig. S5).

2.2.2. Synthesis of $[Sc(Hbidc)(OH)(H_2O)]_n$ (2)

A mixture of H₃bidc (0.0206 g, 0.1 mmol), Sc(NO₃)·6H₂O (0.5 ml, 0.2 M) was added to H₂O (9 ml), KOH (20 μ l, 1 M) in a 23 ml Teflon-lined autoclave and then heated under autogenous pressure at 160 °C for 24 h, then cooled to room temperature under ambient conditions. Colorless block crystals were obtained by filtration and

washed with distilled water, and dried in air. Yield: 80% for **2** (based on Sc(NO₃)·6H₂O). Elemental analysis (%) for **2**: Anal. Calc. C, 38.03; H, 2.46; N, 9.86; Found: C, 37.82; H, 2.55; N, 9.72. IR (KBr pellet, cm⁻¹) for **2** (4000–400 cm⁻¹): 3487 (s), 1793 (w), 1535 (s), 1420 (s), 1269 (m), 1171 (w), 1045 (w), 956 (m), 809 (m), 773 (w), 615(w) (Fig. S6).

2.3. Single crystal X-ray crystallography

Crystallographic data for 1 were collected on a Rigaku R-AXIS RAPID IP diffractometer with graphite-monochromated Mo Ka (0.71073 Å) radiation, while those of **2** were collected on a Bruker SMART APEX-II CCD diffractometer by using graphite-monochromated Mo Ka radiation (0.71073 Å) radiation at a temperature of 296(2) K. All structures were solved by direct methods and refined by full-matrix least-squares fitting on F^2 by the SHELXTL-97 crystallographic software package [18]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms attached to C and N atoms were placed in calculated positions and refined isotropically using a riding model with an $U_{iso}(H)$ equivalent to 1.2 times of $U_{eq}(C)$ or $U_{eq}(N)$. The hydrogen atoms on coordinated water molecules were located in a difference Fourier map and included in the final refinement by use of geometrical constraints or restraints with the O-H distances being fixed at 0.85 Å. Crystal detailed data collection and refinement of CPs 1 and **2** are summarized in Table S1.

2.4. Catalytic experiment

Samples of **1** and **2** were activated at 200 °C for 12 h, soaked in CH_3OH for 24 h and then heated under vacuum at 80 °C for 12 h under vacuum before the reaction. The basic framework of **1** and **2** are retained after activation. For the experiments of catalysis, activated catalyst (0.04 mmol), aldimine (0.14 mmol) and TMSCN (47 µl) in CDCl₃ (2.4 l) were sequentially added to a standard 20 l vial. The reaction mixtures were stirred at room temperature. The reactions were monitored by ¹H NMR spectroscopy and the conversion yield was determined from the ratio of the integral of the product signal in relation to the sum of integrals of all signals (aldimine and product).

3. Results and discussion

3.1. Structural descriptions

3.1.1. Structural description of $[InCl(H_2bidc)_2(H_2O)]_n$ (1)

1 crystallizes in a triclinic $P\overline{1}$ space group. The asymmetric unit of **1** contains one crystallographically unique In^{3+} ion, two H₂bidc⁻ ligands, one coordinated H₂O molecule and one terminal chlorine atom. As shown in Fig. 1a, the In^{3+} ion with six coordinated envi-



Fig. 1. Coordination environment of \ln^{3+} ion in **1**. Symmetry mode: A = 1 - x, -y, -z; B = 1 - x, -y, 1 - z.

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Scheme 1. Coordination modes of the ${\rm H}_3 {\rm bidc}$ ligand. Cps 1 and 2 exhibit I and II modes, respectively.

ronment exhibits approximately octahedral geometry, which is completed by four O atoms of O2A, O5, O7 and O9B (symmetry codes: A = 1 - x, -y, -z; B = 1 - x, -y, 1 - z) from four individual

 H_2 bidc[−] and one O1 atom from one coordinated H_2 O and one terminal chlorine atom. The In–O bond lengths are in the range of 2.1379(17)–2.1971(18) Å, In–Cl is 2.4514(8) Å, the O–In–Cl bond angles range from 85.60(5)° to 169.59(5)° and the O–In–O bond angles range from 84.20(7)° to 175.73(6)° in **1**. All of which are comparable to those of the reported In–CPs [19].

In the structure of **1**, the ligand H_2bidc^- possesses one coordination mode I (Scheme 1). In mode I, every carboxylate group acts in a monodentate mode linking one In^{3+} center. Therefore, each H_2 -bidc⁻ ligand synchronously binds to two In^{3+} ions to form the infinite 1D chains (Fig. 2a). As shown in Table S2, there is a large amount of hydrogen bonds: non-classical bonds (CI···H–N) (Fig. 2b) and common bonds (O–H···O and N–H···O) in compound **1**. The chains parallel with each other to generate a 2D layer via non-classical hydrogen bonds CI1···H1–N1C and CI1···H3–N3I groups (Fig. 2c). H4, H1, O3E and O4D are from benzimidazole rings and carboxyls of different layers, respectively. N4–H4···O3E



Fig. 2. (a) The 1D chain in **1**. (b) Detailed illustration of non-classical hydrogen bonds In–Cl1C···H1–N1 and In–Cl1I···H3–N3 groups in **1**. Symmetry mode: A = -x + 1, -y + 1, -z; I = x, y - 1, z. (c) 2D layer via non-classical hydrogen bonds In–Cl···H–N groups. (d) View of the 3D supramolecular network along the [010] direction, the extensive hydrogen bonds are colored black.



Fig. 3. (a) Coordination environment of Sc³⁺ ion in **2**. (b) Two different helical chains of chiral layers in **2** (hydrogen atoms are omitted for clarity). Symmetry mode: A = 3 - x, -0.5 + y, 1.5 - z; B = 3 - x, 0.5 + y, 1.5 - z; C = 1 + x, y, z.

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and N1–H1…O4D hydrogen bonds link adjacent layers to construct a 3D supramolecular structure. Notably, other hydrogen bonds of O1–H2W…O8F, O1–H1W…O4, N2–H2…O6G, N2–H2…O1G and N3–H3…O9H make the 3D supramolecular more stable (Fig. 2d).

3.1.2. Structural description of $[Sc(Hbidc)(OH)(H_2O)]_n$ (2)

2 is a 2D platelike coordination polymer. **2** crystallizes in a monoclinic $P2_1/c$ space group. There are one crystallographically unique Sc^{3+} ion, one Hbidc^{2–} ligands, one OH[–] and one coordinated H₂O molecule in the asymmetric unit of **2**. As shown in Fig. 3a, the Sc^{3+} ion with six coordinated environment exhibits approximately octahedral geometry, which is completed by three O atoms of O2,

O6B and O7C from three individual Hbidc^{2–}, two O atoms of O4 and O4A (symmetry codes: A = 3 - x, -0.5 + y, 1.5 - z; B = 3 - x, 0.5 + y, 1.5 - z; C = 1 + x, y, z) from two OH[–], one O5W atoms from coordinated H₂O. The Sc–O bond lengths are in the range of 2.068 (2)–2.152(2) Å, the O–Sc–O bond angles range from 85.19(10)° to 176.49(9)°, all of which are in agreement with those of the reported Sc-CPs [20].

In **2**, the two carboxylate groups of H_3 bidc ligand are completely deprotonated, displaying monodentate and bis-monodentate coordination mode II as shown in Scheme 1. It is worth noting that Sc³⁺ ions are linked by C1, C2, C8, C9, O6, O7 of Hbidc²⁻ ligands to generate a left-handed helical chain (L helix) running along the crystallographic 2₁ axis with a pitch of 7.6047 Å, while



Fig. 4. (a) Left chiral layer in **2**. (b) Right chiral layer in **2**. (c) The supramolecular 3D architecture by π - π stacking interactions along the *ac* plane in **2**. (d) π - π stacking interactions in **2** (hydrogen atoms are omitted for clarity).

Table 1

Strecker reaction between *N*-Bn-phenylaldimine and TMSCN Catalyzed by CPs 1 and 2.

	Ph + TMSCN ← Cat. ← HN CDCl₃, r.t. ←	∼Ph `CN	
Entry ^a	Catalyst	Reaction time (h)	Conversion yield (%) ^b
1	1	0.5	20
2	1	5	59
3	1	48	96
4	2	0.5	10
5	2	5	38
6	2	48	86

^a Reaction conditions: aldimine (0.14 mmol), TMSCN (47 µl), catalyst (0.04 mmol), CDCl₃ (2.4 mL) at room temperature.

^b % Conversion calculated by ¹H NMR with aldimines.

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Table 2

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Strecker reaction between aldimines and TMSCN catalyzed by CP **1**.

	Cat. 1		
+ TMSCN	CDCl3, r.t.		
Entry ^a	Aldimine	Reaction time (h)	Conversion yield(%) ^b
1	N Ph	48	97
2	N Ph	48	99
3	Br	48	95
4	H ₃ CO ⁻ Ph	48	64
5	Ph Ph	48	98
6	N Ph	48	98
7	N Ph	48	97
8	CH ₂ CH ₂ CH ₃	168	96
9	Ph	168	77

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Table 2 (continued)



^a Reaction conditions: aldimine (0.14 mmol), TMSCN (47 µl), catalyst (0.04 mmol), CDCl₃ (2.4 l) at room temperature.

^b % Conversion calculated by ¹H NMR with aldimines.

the right-handed screw (R helix) owning the same pitch and components as the former, as shown in Fig. 3b. The torsion angles O6-C9-C1-C2 and O7-C8-C1-C2 are 152.9°, -72.8°, respectively. As shown in Fig. 4a, the different helical chains with identical rotation direction are connected to each other to form left-handed chiral layers. In the same way, Sc³⁺ ions are linked to constitute another right-handed chiral layer, as shown in Fig. 4b. Finally, the adjacent helical layers with the opposite chirality are extended alternately to stack in an ABAB sequence along the *ac* plane and the hydrophobic bulky benzimidazole groups project into the interlamellar regions (Fig. 4c). The adjacent Hbidc²⁻ ligands including one benzene ring and one imidazole ring are parallel nearly. The center distances of the plane-to-plane between benzimidazole ring in the adjoining layers are 3.6824 Å, which indicate the formation of π - π stacking interactions as shown in Fig. 4d. As a result, the 2D layer exists a 3D supramolecular structure. Noteworthily, the benzimidazole ring involved in the π - π stackings arrange in such a way the nine atoms of the ring do not completely overlap those of the other rings. This means the π - π interaction is not "perfect face to face alignment" but "slipped stacking" [21].

3.2. Characterization

Phase purity of **1** and **2** was confirmed by PXRD measurement and PXRD patterns of the as-synthesized samples are in agreement with the simulated ones (Figs. S1 and S2). The difference in intensity may be ascribed to the preferred orientation of the powder samples. TGA analysis was performed on pure single crystal sample of **1** and **2** under air atmosphere with a heating rate of 10 °C min⁻¹ in the range of 25–800 °C. **1** displays a continuous weight loss (76.5 wt.%) in the temperature range of 290–586 °C, which corresponds to the loss of the coordinated water molecules and H₂bidc⁻ ligands in the framework (calc. 75.9 wt.%) (Fig. S3). The TGA plot indicates that **2** releases its OH⁻ groups and coordinated H₂O molecules in the temperature range of 250–400 °C (calc. 12.3 wt. %), forming Sc(Hbidc), which decompose completely in the temperature range of 400–490 °C (calc. 71.8 wt.%) (Fig. S4). Variable-temperature PXRD patterns further indicate that the structures of CPs **1** and **2** are retained up to 250 °C and 300 °C, respectively (Figs. S7 and S8).

The IR spectra of CPs **1** and **2** show the characteristic bands of the carboxylic groups in the usual region around 1384 and 1420 cm^{-1} for the symmetric vibrations and at 1594 and 1535 cm^{-1} for the asymmetric vibrations, respectively (Figs. S5 and S6). The absence of the peak around 1700 cm^{-1} indicates that all carboxyl groups of organic moieties in **1** and **2** are deprotonated, which is consistent with the result of the single-crystal X-ray analysis.

3.3. Catalytic properties

Strecker synthesis has long been considered one of the most direct and viable methods for the synthesis of α -amino acids [22]. Strecker reaction is a Lewis acid or base catalyzed carbon–carbon bond formation. Over years, many compounds have been proved to be excellent catalysts for the Strecker reaction of aldimines; nevertheless, when aldimines were used as substrates, only a few heterogeneous catalysts showed good conversions [23]. Previous studies about CPs have postulated that certain materials exhibit good catalytic activity in such reactions with low loadings, mild temperatures [24].

The CPs **1** and **2** possess available Lewis acid catalytic centers. **1** and **2** were initially evaluated in the Strecker reaction between *N*-Bn-phenylaldimine (Bn = PhCH₂) and TMSCN at room temperature (Table 1, entries 1–6). It was observed that, in contrast to **2**, **1** can catalyze the Strecker reaction with a fairly- high conversion rate. *N*-Bn-aldimine proceeded smoothly in the presence of 28.6 mol% **1** in deuterochloroform (CDCl₃) for 5 h, providing the corresponding α -aminonitrile in 59% conversions (Table 1, entry 2), while **2** catalyzed only provided 38% conversions after 5 h. After 48 h, **1** and **2** achieve 96% and 86% conversions, respectively. This obvious difference in catalytic reactivity may attribute to different metal ions of frameworks. Compared to **2**, **1** exhibits higher catalytic reactivity for the Strecker reaction.



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Fig. 5. Reusability of 1 and 2 catalysts experiments.

To further investigate the generality of catalyst **1**, we also studied the influence of different substitution groups of aldimines on the reaction under same conditions. The experimental results showed that the substituents have an important effect on the Strecker reaction. The substrates containing electron-donating groups, such as 2-bromo and 4-methoxyl, can obtain the product in 99% and 95% after 48 h, respectively (Table 2, entries 2 and 3), whilst, in the case of electron-drawing substrates (4-trifluoromethyl), conversion of the substrate was significantly suppressed (64%, 48 h). In addition, we try to change the substituents' size, however, conversion rate was not affected almost (Table 2, entries 5–7).

Moreover, we also studied the difference among various sizes N-PG (PG = protected group). The experimental results showed that, with increasing size of N-PG, conversion rate dropped dramatically. For example, compared to N-CH₂CH₂CH₃-pheny-laldimine (96%), the conversion rates of N-CH(Ph)₂-phenylaldimine and N-C(Ph)₃-phenylaldimine were 75% and 50%, respectively (Table 2, entries 10 and 11). The significant decrease in conversion rate suggests that large substrates are less likely to access the catalytic sites compared to small ones. The samples of 1 and 2 can be easily recovered from the reaction mixture by filtering and drying.

The stability and recyclability of **1** and **2** were further investigated by using *N*-Bn-(2-bromophenyl)aldimine and *N*-Bn-phenylaldimine as substrates. As shown in Fig. 5, more than 95% conversion of aldimine was still maintained even after four consecutive runs and only a slight decrease was observed in the fifth run. For **2**, the conversion has dropped to 75% in the fourth run. Moreover, the PXRD patterns matched well before and after the catalytic reactions (Fig. S1 and S2).

4. Conclusions

In summary, we reported two highly stable In-based and Scbased CPs **1** and **2**. Such CPs catalysts exhibit rich open Lewis acid sites, and they were then applied as efficient heterogeneous catalysts for the Strecker reaction of aldimines under mild condition. Importantly, **1** shows much higher catalytic activities to the aldimine derivatives with electron-donating groups in comparison to those with electron-withdrawing groups in the catalytic process. With increasing size of *N*-PG, conversions of the aldimines were suppressed obviously. Moreover, the catalyst **1** can be reused up to five times was still maintained stability. The excellent catalytic activity and good stability demonstrate that **1** is an efficient heterogeneous CP catalyst for α -aminonitriles formation at room temperature.

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Appendix A. Supplementary data

CCDC 1554644–1554645 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at https://doi.org/10. 1016/j.poly.2017.10.028.

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